

REMARKS

The rejection of Claims 1-3, 12, 28-29 and 31 under 35 U.S.C. § 102(b) as anticipated by US 4,310,100 (Kunimoto et al), is respectfully traversed. Kunimoto et al discloses a container cap having an easily peelable liner comprising a layer of a hydrocarbon resin or natural resin and a layer containing an epoxy resin and having a peelable interface therebetween, resulting in excellent dust-resisting properties (column 1, lines 54-66). The Examiner finds that the epoxy resin layer of Kunimoto et al is present in order to prevent corrosion and rusting.

In reply, it is the protecting layer 2 therein, not the epoxy resin layer, that is disclosed as relating to corrosion resistance (column 5, line 23ff). More importantly, epoxy resins are not necessarily non-wetting nor does Applicant disclose epoxy resins as non-wetting *per se*. Nevertheless, the rejection is now moot, since the presently-recited material layer requires the presence of an additive, and that the material layer be an outermost layer. In Kunimoto et al, the epoxy resin layer is not an outermost layer.

For all the above reasons, it is respectfully requested that this rejection be withdrawn.

The rejection of Claims 4 and 7-10 under 35 U.S.C. § 103(a) as unpatentable over Kunimoto et al in view of US 5,312,491 (Binter), is respectfully traversed. The disclosures and deficiencies of Kunimoto et al have been discussed above. Binter does not remedy these deficiencies. Binter discloses a rust inhibiting composition comprising an oxime compound as the active rust inhibiting agent, wherein the composition may contain minor amounts of additives (column 4, lines 51-52), including TEFLON (paragraph bridging columns 4 and 5), and a surfactant that is active as an effective wetting agent and leveling aid, preferably ZONYL FSN (column 5, lines 17-28). The reason for the presence of TEFLON is not disclosed.

The Examiner holds that it would have been obvious to employ the TEFLON and ZONYL of Binter to modify the closure cap of Kunimoto et al to prevent corrosion from liquid on the cap.

In reply, neither TEFLON nor ZONYL is described in Binter as imparting any kind of corrosion prevention. Thus, there would have been no reason to combine Kunimoto et al and Binter. Additionally, even if the TEFLON and ZONYL were added to the epoxy resin layer of Kunimoto et al, the result would not be the presently-claimed invention.

For all the above reasons, it is respectfully requested that this rejection be withdrawn.

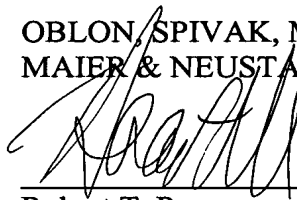
The rejection of Claims 28-31 under 35 U.S.C. § 103 as unpatentable over US 3,910,445 (Garza et al) in view of Kunimoto et al, is respectfully traversed. As discussed above, Kunimoto et al does not disclose a non-wetting layer. Therefore, even if the epoxy resin layer of Kunimoto et al were employed to modify the crown cap of Garza et al, the result would still not be the presently-claimed invention. Accordingly, it is respectfully requested that this rejection be withdrawn.

The objection to the non-capitalization of trademarks is now moot in view of the above-discussed amendment. Accordingly, it is respectfully requested that the objection be withdrawn.

Applicant gratefully acknowledges the Examiner's indication of allowability of the subject matter of Claims 5-6 and 11. Nevertheless, Applicant respectfully submits that all of the presently pending and active claims in this application are now in immediate condition for allowance. Accordingly, the Examiner is respectfully requested to rejoin the non-elected method claims, and in the absence of further grounds of rejection, pass this application to issue with all pending claims.

Respectfully submitted,

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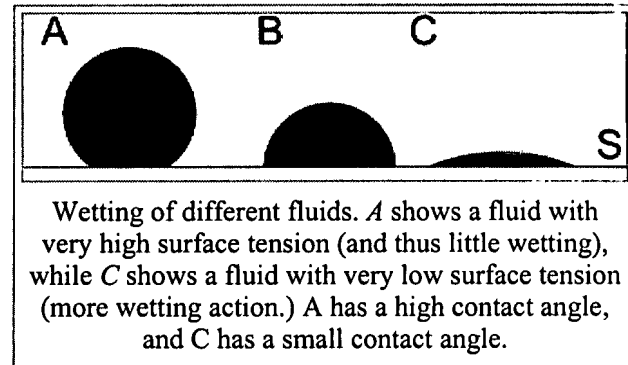
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Wetting

From Wikipedia, the free encyclopedia

Wetting is the contact between a fluid and a surface, when the two are brought into contact. When a liquid has a high surface tension (strong internal bonds), it will form a droplet, whereas a liquid with low surface tension will spread out over a greater area (bonding to the surface). On the other hand, if a surface has a high surface energy (or surface tension), a drop will spread, or wet, the surface. If the surface has a low surface energy, a droplet will form. This phenomenon is a result of the minimization of interfacial energy. If the surface has a high energy, it will want to be covered with a liquid because this interface will lower its energy, and so on.



The primary measurement to determine wettability is a contact angle measurement. This measures the angle between the surface and the surface of a liquid droplet on the surface. For example, a droplet would have a high contact angle, but a liquid spread on the surface would have a small one. The contact angle θ and the surface energies of the materials involved are related by the Young–Dupré equation

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad [1]$$

where γ is the surface tension between two substances and S, V, and L correspond to the solid, vapor, and liquid substances in a contact angle experiment respectively.

A contact angle of 90° or greater generally characterizes a surface as not-wettable, and one less than 90° means that the surface is wettable. In the context of water, a wettable surface may also be termed hydrophilic and a non-wettable surface hydrophobic. Superhydrophobic surfaces have contact angles greater than 150°, showing almost no contact between the liquid drop and the surface. This is sometimes referred to as the "Lotus effect". This characteristic of spreading out over a greater area is sometimes called 'wetting action' when discussing solders and soldering.

Wetting is often an important factor in the bonding (adherence) of two materials. It is also the basis for capillary action, the ability of a narrow tube to draw a liquid, even against the force of gravity.

The shape of a drop is roughly a spherical cap.

See also

- Dewetting
- Sessile drop technique

References

- [^] <http://www.iop.org/EJ/article/0953-8984/10/27/001/cm1002711.html>

Retrieved from "<http://en.wikipedia.org/wiki/Wetting>"

Category: Fluid mechanics

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Langmuir-Blodgett Instruments Tensiometers Goniometers Surface Chemistry



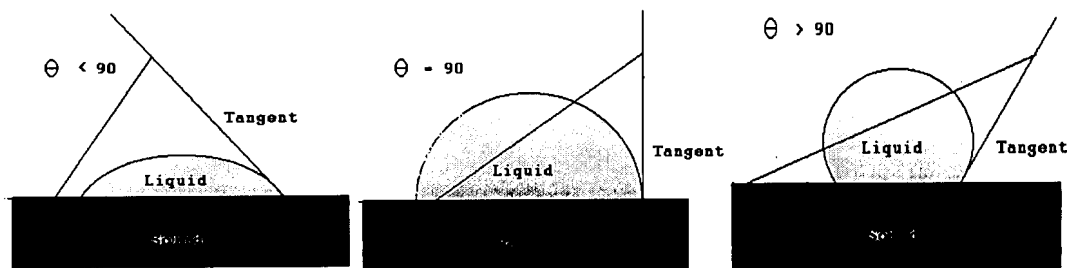
Contact Angles AN #102



This application note provides a brief introduction to the use and measurement of contact angles. The techniques used for measurement are discussed and compared.

What is contact angle?

Contact angle, θ , is a quantitative measure of the wetting of a solid by a liquid. It is defined geometrically as the angle formed by a liquid at the three phase boundary where a liquid, gas and solid intersect as shown below:



It can be seen from this figure that low values of θ indicate that the liquid spreads, or wets well, while high values indicate poor wetting. If the angle θ is less than 90 the liquid is said to wet the solid. If it is greater than 90 it is said to be non-wetting. A zero contact angle represents complete wetting.

The measurement of a single static contact angle to characterize the interaction is no longer thought to be adequate. For any given solid/ liquid interaction there exists a range of contact angles which may be found. The value of static contact angles are found to depend on the recent history of the interaction. When the drop has recently expanded the angle is said to represent the 'advanced' contact angle. When the drop has recently contracted the angle is said to represent the 'receded' contact angle. These angles fall within a range with advanced angles approaching a maximum value and receded angles approaching a minimum value.

If the three phase(liquid/solid/vapor) boundary is in actual motion the angles produced are called Dynamic Contact Angles and are referred to as 'advancing' and 'receding' angles. The difference between 'advanced' and 'advancing', 'receded' and 'receding' is that in the static case motion is incipient in the dynamic case motion is actual. Dynamic contact angles may be assayed at various rates of speed. Dynamic contact angles measured at low velocities should be equal to properly measured static angles.

Hysteresis

The difference between the maximum(advanced/advancing) and minimum(receded/receding) contact angle values is called the contact angle hysteresis. A great deal of research has gone into analysis of the significance of hysteresis. It has been used to help characterize surface heterogeneity, roughness and mobility. Briefly, for surfaces which are not homogeneous there will exist domains on the surface which present barriers to the motion of the contact line. For the case of chemical heterogeneity these domains represent areas with different contact angles than the surrounding surface. For example when wetting with water, hydrophobic domains will pin the motion of the contact line as the liquid advances thus increasing the contact angles. When the water recedes the hydrophilic domains will hold back the draining motion of the contact line thus decreasing the contact angle. From this analysis it can be seen that, when testing with water, advancing angles will be sensitive to the hydrophobic domains and receding angles will characterize the hydrophilic domains on the surface.

For situations in which surface roughness generates hysteresis the actual microscopic variations of slope in the surface create the barriers which pin the motion of the contact line and alter the macroscopic contact angles. There has been a great deal of research investigating the significance of hysteresis and you are recommended to the papers cited at the end of this note for further details.

Contact angle can also be considered in terms of the thermodynamics of the materials involved. This analysis involves the interfacial free energies between the three phases and is given by:

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl}$$

where γ_{lv} , γ_{sv} and γ_{sl} refer to the interfacial energies of the liquid/vapor, solid/vapor and solid/liquid interfaces.

How is contact angle measured?

Two different approaches are commonly used to measure contact angles of non-porous solids, goniometry and tensiometry. Goniometry involves the observation of a sessile drop of test liquid on a solid substrate. Tensiometry involves measuring the forces of interaction as a solid is contacted with a test liquid. Both techniques are described below with comments on the choice of either technique for particular research applications.

In the case of porous solids, powders and fabrics another approach is commonly used. This technique involves using a tensiometer, such as the KSV Sigma 70, and the Washburn method. It is the method of choice when your sample contains a porous architecture which absorbs the wetting liquid. It is described briefly below and more completely in Application Note # 104.

Goniometry

Analysis of the shape of a drop of test liquid placed on a solid is the basis for goniometry. The basic elements of a goniometer include a light source, sample stage, lens and image capture. Contact angle can be assessed directly by measuring the angle formed between the solid and the tangent to the drop surface.

The production of drops with advanced and receded edges involves one of two strategies. Drops can be made to have advanced edges by addition of liquid. Receded edges may be produced by allowing sufficient evaporation or by withdrawing liquid from the drop. Alternately, both advanced and receded edges are produced when the stage on which the solid is held is tilted to the point of incipient motion. Using an instrument with high speed image capture capabilities shapes of drops in motion may be analyzed.

KSV Instruments supplies two instruments for goniometry, the CAM100 and CAM 200. The CAM100 uses a 50mm USB camera for image capture. The CAM200 instruments uses a high speed CCD camera for image capture. The images are analyzed with computer software.

Advantages

Goniometry can be used in many situations where tensiometry cannot. You can use a great variety of solid substrates provided they have a relatively flat portion for testing and can fit on the stage of the instrument. Substrates with regular curvature, such as contact lenses are also easily analyzed.

Testing can be done using very small quantities of liquid. It is also easy to test high temperature liquids such as polymer melts.

Limitations

The assignment of the tangent line which will define the contact angle is a factor which can limit the reproducibility of contact angle measurements. Conventional goniometry relies on the consistency of the operator in the assignment of the tangent line. This can lead to significant error, especially subjective error between multiple users. KSV Instruments' CAM 200 and CAM100 remove this problem by using computer analysis of the drop shape to generate consistent contact angle data.

The conditions which produce advanced and receded angles are sometimes difficult to reproduce. Although drops in motion can produce data on dynamic contact angles the velocity of motion cannot be controlled. It is also less suited, when compared to tensiometry, to analysis of the effects of wetting on changes in contact angle.

In addition the amount of surface sampled for each measurement is limited and multiple measurements should be used to characterize a surface. Fibers are not easily studied by goniometry.

Tensiometry

The tensiometric method for measuring contact angles measures the forces that are present when a sample of solid is brought into contact with a test liquid. If the forces of interaction, geometry of the solid and surface tension of the liquid are known the contact angle may be calculated. The user first makes a measurement of the surface tension of the liquid using either a Wilhelmy plate or DuNouy ring. The sample of the solid to be tested is then hung on the balance and tared. The liquid is then raised to contact the solid. When the solid contacts the liquid the change in forces is detected and your Sigma70 registers this elevation as zero depth of immersion. As the solid is pushed into the liquid the forces on the balance are recorded. The forces on the balance are

$$F_{\text{total}} = \text{wetting force} + \text{weight of probe} - \text{buoyancy}$$

Your Sigma70 has tared the weight of the probe and can remove the effects of the buoyancy force by extrapolating the graph back to zero depth of immersion. The remaining component force is the wetting force which is defined as:

$$\text{Wetting force} = \gamma_{LV} P \cos\theta$$

where γ_{LV} is the liquid surface tension, P is the perimeter of the probe and θ is the contact angle. Thus at any depth data is received which can be used to calculate contact angle. This contact angle, which is obtained from data generated as the probe advances into the liquid, is the advancing contact angle. The sample is immersed to a set depth and the process is reversed. As the probe retreats from the liquid data collected is used to calculate the receding contact angle.

Advantages

The use of tensiometry for measurement of contact angle has several advantages over conventional goniometry. At any point on the immersion graph, all points along the perimeter of the solid at that depth contribute to the force measurement recorded. Thus the force used to calculate θ at any given depth of immersion is already an averaged value. You may calculate an averaged value for the entire length of the sample or average any part of the immersion graph data to assay changes in contact angle along the length of the sample.

This technique allows the user to analyze contact angles produced from wetting over an entire range of velocities from static to rapid wetting. Because the contact angles are determined from the forces measured by the instrument there is no possibility of subjective error.

The graphs produced by this technique are very useful in studying hysteresis. Variations of contact angles, both advancing and receding, for the entire length of the sample tested are visualized on the same graph. In addition variations generated over multiple wetting/dewetting cycles can yield information on changes caused by wetting (such as absorption or surface reorientation).

Analysis of fibers, very problematic for goniometry, is handled easily by your tensiometer.

Limitations

There are two major limitations for the application of this technique. Firstly the user must have enough of the liquid being tested available so that he can immerse a portion of his solid in it. Secondly the solid in question must be available in samples which meet the following constraints. The sample must be formed or cut in a regular geometry such that it has a constant perimeter over a portion of its length. Rods, plates or fibers of known perimeter are ideal. The sample must have the same surface on all sides which contact the liquid. The sample must also be small enough so that it can be hung on the microbalance of your Sigma70.

It is also more difficult to use this technique in systems which are measured at high temperatures. Temperatures at or below 100 ° C are easily handled but for measurements above this range goniometry is recommended.

Washburn Method

This method is chosen when the solid sample to be tested contains a porous architecture which leads to absorption of the wetting liquid. The solid is brought into contact with the testing liquid and the mass of liquid absorbed into the solid is measured as a function of time. The amount absorbed is a function of the viscosity, density and surface tension of the liquid, the material constant of the solid, and the contact angle of the interaction. If the viscosity, density and surface tension of the liquid are known the material constant and contact angle can be solved for. KSV instruments produces two instruments capable of finding contact angles via the Washburn technique, the Sigma 70 and LPR 902. See Application Note #104 for details.

Utilization of Contact Angle Data:

The primary focus of contact angle studies is in assessing the wetting characteristics of solid/liquid interactions. Contact angle is commonly used as the most direct measure of wetting. Other experimental parameters may be derived directly from contact angle and surface tension results. Some examples are:

Work of Adhesion: defined as the work required to separate the liquid and solid phases, or the negative free energy associated with the adhesion of the solid and liquid phases. Used to express the strength of the interaction between the two phases. It is given by the Young-Dupre equation as:

$$W_a = \gamma (1 + \cos \theta)$$

Work of Cohesion: defined as the work required to separate a liquid into two parts, it is a measure of the strength of molecular interactions within the liquid. It is given by;

$$W_c = 2 \gamma$$

Work of Spreading: the negative free energy associated with spreading liquid over solid surface. Also referred to as Spreading Coefficient it is given as:

$$W_s = \gamma (\cos \theta - 1)$$

Wetting Tension: a measurement of force/length defined as:

$$\tau = F_w / P = \gamma_{LV} \cos \theta$$

This value, wetting force normalized for length, also represents the product of the cosine of the contact angle and the surface tension. It allows for a characterization of the strength of the wetting interaction without separate measurement of surface tension. Most helpful in situations, such as multicomponent systems, where surface tension at interface may not equal equilibrium surface tension. Also referred to as Adhesion Tension or Work of Wetting.

Characterization of the Solid Surface

Measurements of surface tension yield data which directly reflect thermodynamic characteristics of the liquid tested. Measurement of contact angles yield data which reflect the thermodynamics of a liquid/solid interaction. If you wish to characterize the wetting behavior of a particular liquid/solid pair you only need to report the contact angle. It is possible to characterize the wettability of your solid in a more general way. Various methods are used but the same basic principle applies for each. The solid is tested against a series of liquids and contact angles are measured. Calculations based on these measurements produce a parameter(critical surface tension, surface free energy,etc) which quantifies a characteristic of the solid which mediates wetting. Two basic approaches are covered here

Critical Surface Tension: Using a series of homologous liquids of differing surface tensions a graph of $\cos\theta$ vs γ is produced. It will be found that the data form a line which approaches $\cos\theta = 1$ at a given value of γ . This is the maximal surface tension of a liquid which may completely wet your solid. This value, called the critical surface tension, can be used to characterize your solid surface. See references for details on procedure and limitations.

Free Surface Energy: Another way to characterize a solid surface is by calculating free surface energy, also

referred to as solid surface tension. This approach involves testing the solid against a series of well characterized wetting liquids. The liquids used must be characterized such that the polar and dispersive components of their surface tensions are known. The relevant equation is given by Owens and Wendt as:

$$\gamma_l (1 + \cos \theta) / (\gamma_{ld})^{1/2} = (\gamma_{sp})^{1/2} [(\gamma_{lp})^{1/2} / (\gamma_{ld})^{1/2}] + (\gamma_{sd})^{1/2}$$

where θ is the contact angle, γ_l is liquid surface tension and γ_s is the solid surface tension, or free energy. The addition of d and p in the subscripts refer to the dispersive and polar components of each. The form of the equation is of the type $y = mx + b$. You can graph $(\gamma_{lp})^{1/2} / (\gamma_{ld})^{1/2}$ vs $\gamma_l (1 + \cos \theta) / (\gamma_{ld})^{1/2}$. The slope will be $(\gamma_{sp})^{1/2}$ and the y-intercept will be $(\gamma_{sd})^{1/2}$. The total free surface energy is merely the sum of its two component forces.

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